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Chiral cyclometalation of 6-(1-phenylbenzyl)-2,2'-bipyridine

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Abstract

A new bipyridine ligand, 6-(1-phenylbenzyl)-2,2'-bipyridine, has been prepared by a multistep synthesis starting from the corresponding substituted pyridine. The coordinating properties of the new ligand have been tested with two d^8 metal ions, Pt(II) and Pd(II), to give the cyclometalated complexes [Pt(N,N,C)Cl] and [Pd(N,N,C)Cl], where N,N,C is a terdentate deprotonated bipyridine containing a new stereogenic carbon atom directly generated by C-H bond activation. The single-crystal of the platinum complex has been solved by X-ray diffraction. DFT calculations confirm the presence of a $Pr^{\cdots}H$ interaction that stabilizes one of the two possible conformers by 14.7 kJ/mol for Pt and 12.9 kJ/mol for Pd. The energy barrier to pass from one conformer to the other is 25.4 and 23.8 kJ/mol respectively.

Under different reaction conditions, regioselective activation of a pyridine C-H bond gave the less common cyclometalated rollover complex [Pt(L-H)Me(DMSO)], which was isolated and characterised.

Keywords: cyclometalation, C-H bond activation, metal-hydrogen interactions

Introduction

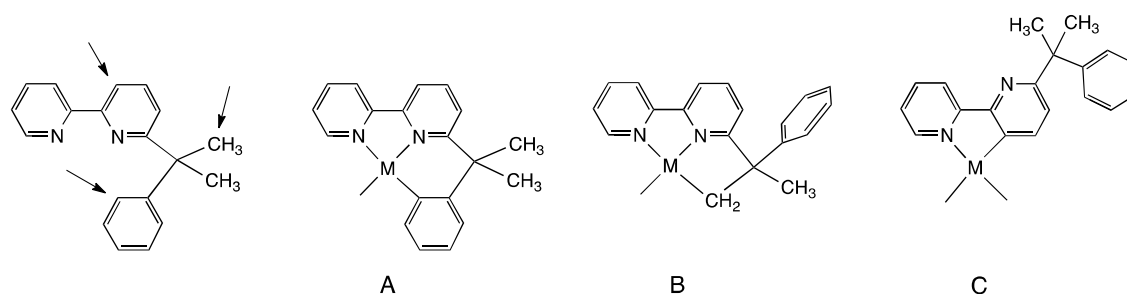
Cyclometalation is one of the most popular organometallic reactions: it provides a robust method for the regioselective activation of C-H bonds and allows for the synthesis of particularly stable organometallic compounds, the so-called cyclometalated complexes.¹

The enhanced stability of cyclometalated complexes, due to chelation, plays an important role in their wide application potential in several fields, ranging from organic transformations to catalysis, materials science and biomedicine. In particular, cyclometalated complexes of d^8 metal ions, such as Pt(II), Pd(II) and Au(III) have been studied as sensors, catalysts, anticancer agents, light-emitting diodes, molecular switches, photovoltaic cells, liquid crystalline materials.^{1,2}

This class of compounds include classical bidentate complexes (such as those derived from 2-phenylpyridine),^{1,2} non-classical species (such as those derived from rollover cyclometalation),³ symmetrical terdentate complexes (the so-called pincer complexes, e.g. N,C,N),⁴ and un-symmetrical terdentate complexes, such as those derived from substituted 2,2'-bipyridines⁵ or di-imines.⁶

Terdentate ligands usually offer an enhanced structural versatility, allowing fine tuning of stereo-electronic properties, promoting reaction steps in catalytic cycles.⁷

Regioselectivity in C-H bond activation is not a trivial point, and competition between several positions may occur. The driving force of these reactions is not fully understood, and subtle factors can drive the reaction towards unexpected results. As an example, Pd(II) and Pt(II) complexes can activate 6-dimethylbenzyl-2,2'-bipyridine in three different positions to give a terdentate complex with [5,6] fused rings by $C(sp^2)$ -H bond activation or with [5,5] fused rings by $C(sp^3)$ -H bond activation, and a cyclometalated rollover complex by $C(sp^2)$ -H bond on a pyridine ring (Chart 1, species A, B and C, respectively).^{3c,8}



M = Pd and/or Pt

Chart 1

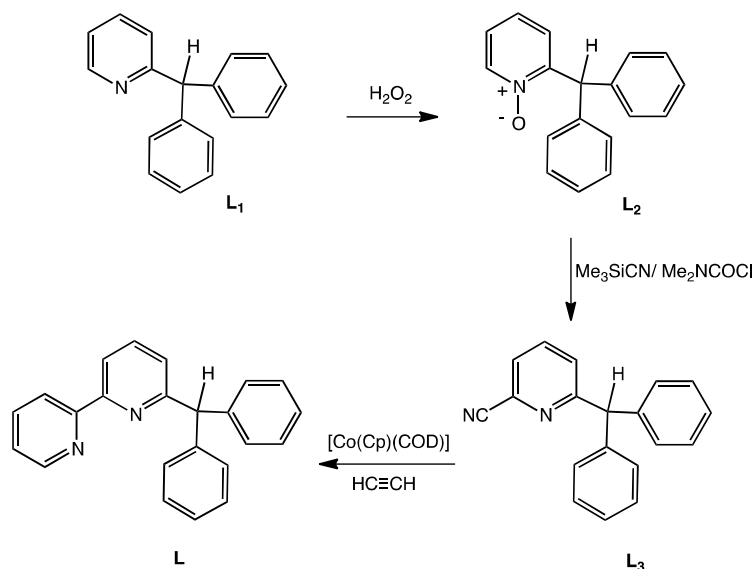
On the whole, the majority of studies has been devoted to five-membered cyclometalated species, usually considered more stable than the six-membered one.^{2,9} However, although less common, six-membered cyclometalates have raised considerable interest.

A prominent case of six-membered ring cyclisation is given by 2-benzylpyridines and 6-benzyl-2,2'-bipyridines.¹⁰ The metallacycle in these complexes adopts a six-membered boat conformation, as shown, *inter alia*, by X-ray analysis. The substituent on the benzylic carbon is able to occupy a pseudo-axial position so that a C-H bond is in close proximity to the metal, the nature of these kinds of interactions is still unclear and has been debated for a long time.¹¹ These interactions can exert subtle effects on compound stability as illustrated by the reactivity of platinum(II) hydrides containing cyclometalated 6-benzylbipyridine ligands.¹² Following our continued efforts to understand the properties of cyclometalated derivatives of d⁸ metal ions with 2,2'-bipyridines,^{10, 13} we have synthesized a new ligand, 6-(1-phenylbenzyl)-2,2'-bipyridine, and investigated its behaviour with Pt(II) and Pd(II) ions. This ligand is potentially able to form terdentate N,N,C cyclometalated complexes with [5,6] fused rings, and a suitably orientated phenyl substituent on the benzylic carbon atom can furnish stabilization.

Results and discussion

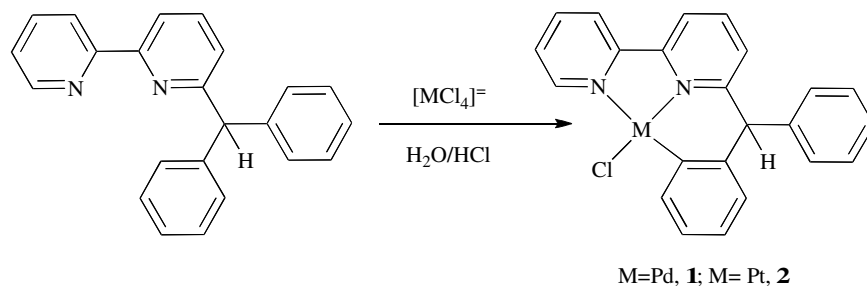
The ligand

The ligand 6-(1-phenylbenzyl)-2,2'-bipyridine, L, has been synthesized using a 3 step sequence starting from the corresponding pyridine: 2-(1-phenylbenzyl)pyridine, L₁. Oxidation of L₁ with hydrogen peroxide gave 2-(1-phenylbenzyl)pyridine-N-oxide, L₂, from which the corresponding nitrile, 6-cyano-2-(1-phenylbenzyl)pyridine, L₃, was obtained by reaction with trimethylsilyl cyanide and N,N-dimethylcarbonyl chloride.¹⁴ The final step consists in a co-cyclotrimerization reaction with acetylene in the presence of Bönnemann catalyst, [Co(Cp)(COD)] (Cp = cyclopentadiene, COD = 1,5-cyclooctadiene).¹⁵ The full reaction sequence is reported in Scheme 1.



The ligand **L** is reported here for the first time, and has been characterized by means of ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum of **L** shows three spin systems corresponding to the monosubstituted external pyridine ring (4H), the disubstituted inner pyridine (3H), and two equivalent phenyl rings ($2 \times 5\text{H}$). In addition, a singlet at δ 5.74 ppm is attributable to the benzylic hydrogen. The H_6 signal, at δ 8.66 ppm, is, as usual, the most deshielded one. ^1H NMR assignment is reported in Table 1. In addition, a ^1H - ^{13}C HSQC NMR experiment enabled a complete ^{13}C NMR assignment.

The organometallic reactivity of **L** has been investigated with two d^8 transition metals: Pd(II) and Pt(II). Reaction of **L** with Na_2PdCl_4 in a $\text{H}_2\text{O}/\text{HCl}$ mixture gives high yields of the cyclometalated complex $[\text{Pd}(\text{L-H})\text{Cl}]$, **1**, where the deprotonated bipyridine acts as a terdentate monoanionic ligand with an N,N,C sequence. Worth of note, the C-H bond activation occurs even at room temperature, and the reaction directly generates a stereogenic carbon atom.

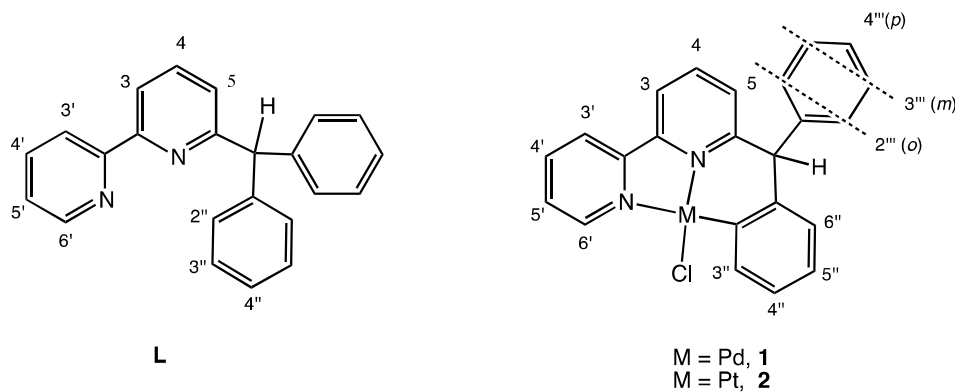


Complex **1** has been thoroughly characterised by means of 1D and 2D ^1H NMR spectroscopy. The ^1H NMR spectrum shows 16 aromatic protons in place of the original 17 of the ligand. Analysis of the 2D COSY spectrum allowed us to fully assign ^1H signals, showing that the missing proton is, as expected, one of the *ortho* hydrogens of the phenyl rings (Scheme 2). As a consequence, the two phenyl groups are no longer equivalent.

Table 1. ^1H NMR data^a

	L	1	2
$\text{CH}(\text{Ph})_2$	5.74	5.75	5.67
H ₃	8.31	8.04-8.07 ^b	8.00-8.06 ^b
H ₄	7.79	8.08	8.12
H ₅	7.22	7.84	7.93 (10)
H _{3'}	8.37	8.04-8.07 ^b	8.00-8.06 ^b
H _{4'}	7.80	8.04-8.07 ^b	8.11
H _{5'}	7.26	7.61	7.68
H _{6'}	8.66	9.31	9.62 (ca 13)
H _{2''}	7.2-7.4 ^b	-	-
H _{3''}	7.2-7.4 ^b	8.01	7.79 (27)
H _{4''}	7.2-7.4 ^b	6.98	7.26-6.98 ^b
H _{5''}		7.07	7.26-6.98 ^b
H _{6''}		7.22	7.26-6.98 ^b
H _{2'''}		7.57	7.52
H _{3'''}		7.29	7.21
H _{4'''}		7.20	7.26-6.98 ^b

a) Pt-H coupling constants in parentheses; b) multiplet of overlapping signals.

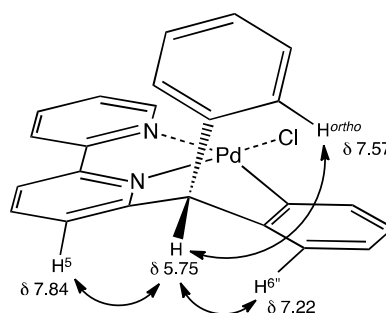


Scheme 2

In addition, the spectrum shows a singlet at δ 5.75 due to the benzylic proton, almost superimposable to that of the ligand. The $H_{6'}$ signal (δ 9.31 ppm) is strongly deshielded with respect to the free ligand ($\Delta\delta = 0.65$ ppm); this shift has been previously observed in related complexes and reflects the through-space influence of the adjacent chloride ligand.^{16, 10c}

A 1H NOE-difference experiment showed that irradiation of the singlet at δ 5.75 ppm (benzylic CH) gave enhancement at δ 7.22 ($H_{6''}$) and 7.84 ppm (H_5), and, to a lesser extent, at δ 7.57 ppm (phenyl *ortho* protons, see Scheme 3). Strong interactions of the benzylic hydrogen with H_5 and $H_{6''}$ should not be present in the case of a rigid conformation of the six-membered ring with benzylic hydrogen in an axial position.

It should also be noted that the H_{ortho} protons are deshielded with respect to the free ligand (7.57 ppm vs ca 7.3 ppm), likely reflecting a through-space influence of the metal centre.



Scheme 3. Noe interactions in complex **1**. For clarity, the interaction with only one *ortho* proton is reported

Using K_2PtCl_4 , cyclometalation occurs only at higher temperature. Prolonged reaction times at 100 °C are required to isolate good yields of the terdentate complex $[Pt(L-H)Cl]$, **2**, analogous to **1**. Complex **2** was thoroughly characterised by analytical and spectroscopic methods both in solution (NMR spectroscopy) and in the solid state (microanalyses and X-ray diffraction).

Also in this case 2D NMR spectroscopy helped us in the complete assignment of the 1H NMR signals (see the Experimental Section and Table 1). The N,N,C terdentate coordination in solution is confirmed by the signals of $H_{6'}$, H_5 and $H_{3''}$. The $H_{6'}$ signal is strongly deshielded, 9.62 ppm, and coupled to platinum; the coordination shift, $\Delta\delta = 0.96$ ppm, greater than in complex **1**, reflects the proximity to the chloride ligand, and the presence of satellites ($^3J_{Pt-H}$ ca 13 Hz) confirms coordination of the external nitrogen atom. The small value of this coupling

is attributable to the N-Pt-C *trans* arrangement and to the high *trans*-influence of carbon.¹⁷ As for the central pyridine, a double doublet centred at 7.93 ppm, assigned to H₅, shows satellites due to ¹⁹⁵Pt-¹H coupling, ⁴J_{Pt-H} = 10 Hz, confirming coordination of the central nitrogen atom. Finally, the signal at 7.79 ppm, due to the H_{3''} proton, is coupled to the platinum atom, ³J_{Pt-H} = 27 Hz, confirming coordination of the adjacent C_{2''} atom and terdentate coordination.

The structure in the solid state of the cyclometalated derivative [Pt(L-H)Cl], **2**, has been solved by X-ray diffraction. An ORTEP view of **2** is shown in Figure 1, along with selected bond distances and angles.

The platinum atom in **2** displays a distorted square planar coordination, with C11 and C14 lying -0.169 and + 0.403 Å, respectively, above and below the plane defined by Pt1, N1 and N7. At variance, Pt1, C11, N1 and N7 may be considered almost coplanar (maximum deviations from their best plane being 0.0526(11) and -0.0299(6) Å for Pt1 and N7, respectively), with the C14 atom displaced 0.492 Å out of this plane.

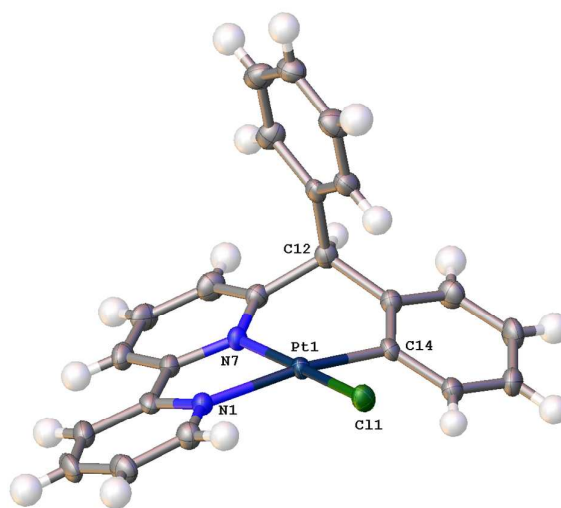
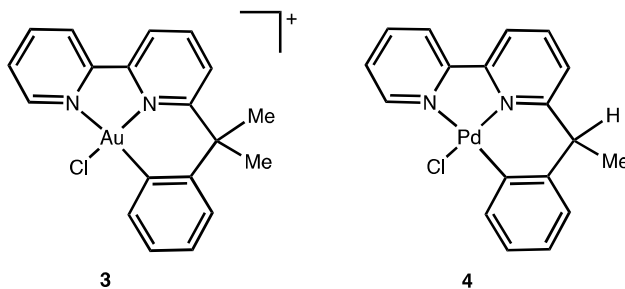


Figure 1. Solid state structure of **2** with only key atoms labelled. Solvent water has been removed for clarity and thermal ellipsoids are drawn at 50% probability level. Selected bond lengths (Å) and angles (°): C11-Pt1 2.3144(9); N1-Pt1 2.101(3); Pt1-N7 2.000(3); Pt1-C14 2.012(4); N1-Pt1-C11 94.37(9); N7-Pt1-C11 173.02(9); N7-Pt1-N1 80.03(12); N7-Pt1-C14 93.05(13); C14-Pt1-C11 93.26(11); C14-Pt1-N1 166.58(13).

The dihedral angle between the Pt1-N1-N7 and Pt1-C11-C14 planes is 12.09°. The distortion from the ideal square-planar geometry is attributable to the limited flexibility of the N,N,C ligand. A similar distortion has been previously found in two similar cyclometalated

complexes, $[\text{Au}(\text{L}')\text{Cl}]^+$ ($\text{HL}' = \text{N}_2\text{C}_{10}\text{H}_7(\text{C}(\text{CH}_3)_2\text{Ph})\text{-6}$, **3**)¹⁸ and $[\text{Pd}(\text{L}'')\text{Cl}]$ ($\text{HL}'' = \text{N}_2\text{C}_{10}\text{H}_7(\text{CHMePh})\text{-6}$, **4**)^{10a} (11.2(6) and 16°, respectively). The similarity with the present terdentate ligand is that in L' the benzylic carbon atom bears two methyl groups, whereas in L'' has one methyl and one hydrogen.



In addition, the similarity of the covalent radii of Pt(II), Pd(II) and Au(III), allows a comparison between the metal-ligand distances in **2**, **3** and **4**. Thus, the Pt1-N1, Pt1-N2 and Pt1-C14 bond lengths in **2** (2.102(3), 1.999(3), 2.013(3) Å, respectively) are comparable to those previously found in **3** and **4** (2.121(5), 2.009(4) and 2.009(6) Å in **3**; 2.119(4), 2.008(4) and 1.980(6) Å in **4**). The elongation of the metal-N(1) bond is obviously due to the *trans* influence of the C14 atom. The two bite angles of the terdentate ligand in **2** N1-Pt1-N7 and N7-Pt1-C14, 80.0(1) and 93.0(1)° respectively, are similar to those found in **3** (79.5(2) and 91.3(2)°) and **4** (79.5(2) and 91.9(2)°). The Pt1-Cl1 bond length, 2.314(9) Å, is typical.

The six-membered metallacycle adopts a boat conformation, with N7, C11, C13 and C14 atoms essentially coplanar (maximum deviations from their mean plane being -0.0201(19) and +0.0196(19) Å for C11 and C13, respectively), with Pt1 and C12 lying above this mean plane, respectively by 0.4674(52) and 0.5511(53) Å.

The non-metalated phenyl points towards the metal, with one *ortho* hydrogen at 3.1186 Å from the platinum, a distance slightly greater than those previously found in similar systems with long-range metal-H interactions.

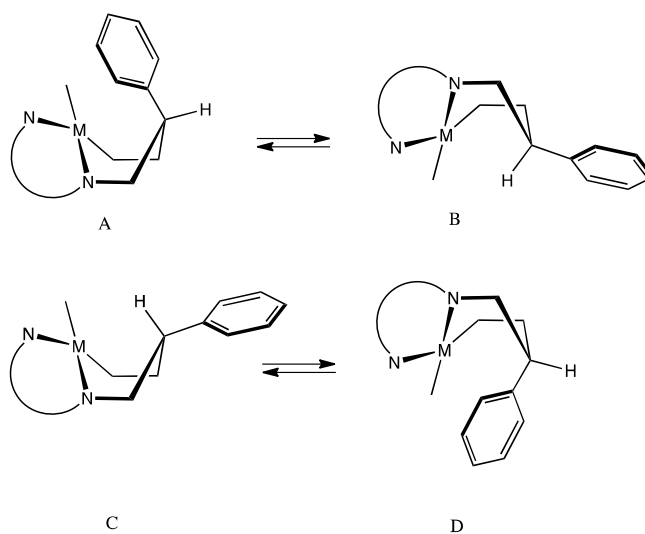
Several methods for the evaluation of van der Waals radii have been proposed,¹⁹ though there has been some debate on their usefulness for determining the existence of weak interactions.²⁰ In the case of platinum, values ranging from 1.72 to 2.39 Å were reported.²¹ Assuming a van der Waals radius for hydrogen of 1.20 Å, the Pt-H distance of 3.1186 Å in complex **2** is shorter than the sum of the van der Waals' radii and may suggest the presence of a weak interaction, even if this distance lies above the range usually reported for a Pt-H interactions

(*ca* 2.3-2.9 Å).

Boat conformation in solution

As shown by the X-ray study of complex **2**, the six-membered ring adopts a boat conformation in the solid state. Such a conformation is likely to be present for complexes **1** and **2** even in solution, as the H_{ortho} protons of the non-metalated phenyl are strongly deshielded in the 1H NMR spectra of both complexes with respect to the free ligand, reflecting a through-space influence of the metal. In contrast, the signals for the benzylic hydrogens are almost superimposable. These data suggest that in solution the phenyl group may approach the metal in a pseudo-axial position (A or D in Scheme 4), even if the six-membered ring is probably fluxional in solution, in the NMR time scale, giving a mediated situation in the spectra. A low temperature 1H NMR spectrum of **1** in CD_2Cl_2 ($T = 183K$) did not show significant differences with the room temperature spectrum.

The cyclometalation process creates a stereogenic benzylic carbon atom producing a pair of enantiomers (*e.g.* A and C in Scheme 4). In addition, the boat conformation of the six-membered metallacycle adds a further element of chirality, to give four stereoisomers, as two couples of enantiomers (Scheme 4: A, D; B, C), possibly in rapid interconversion in solution.



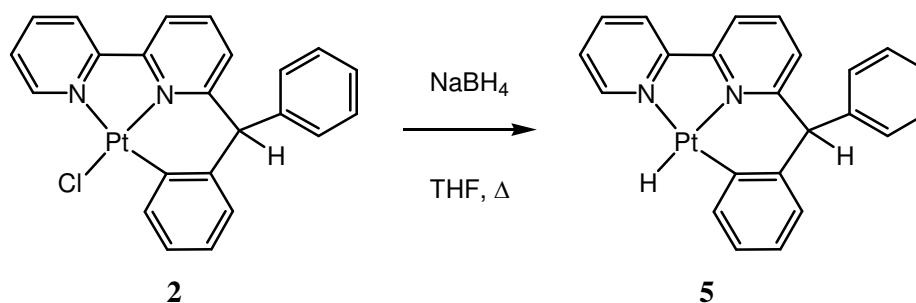
Scheme 4

M--H--C contacts in axial position of square planar d^8 transition metal complexes ($M = Pd, Pt, Au$) have received much attention in the last decades.¹¹ Different kinds of interactions have

been described, classified in various ways, such as a) anagostic (repulsive 3c–4e), b) hydrogen-bond (attractive 3c–4e), c) preagostic (or pregostic, attractive 3c–2e), σ -agostic (attractive, 3c–2e);²² with the metal acting as an acceptor or a donor center. X-ray, NMR and IR methods have been used to discriminate these interactions.

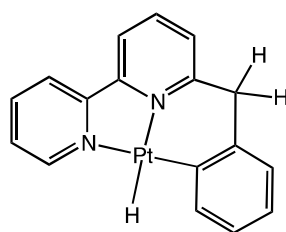
Very recently,²⁰ a characterization based on high pressure IR and X-ray studies demonstrated that the metal may display local Lewis acidic sites in axial direction in order to establish weakly *attractive* 3c-2e $M\cdots H-C$ agostic interactions and suggests that using 1H NMR shifts as a major criterion in the classification of the interaction can be dubious.

The presence of such weak interactions in N,N,C cyclometalated platinum(II) complexes has been shown to have a dramatic impact on the stability and reactivity of the corresponding hydrides. For this reason, we reacted complex **2** with $NaBH_4$ in THF to give the hydrido complex $[Pt(L-H)H]$, **5**, with reasonable yields (ca 45 %).



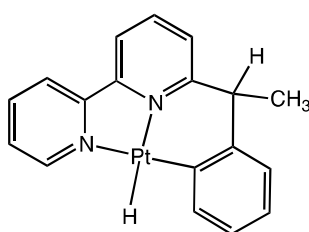
Complex **5** was characterized by means of analytical and spectroscopic methods. In particular, in the 1H NMR spectrum the hydride signal, at -13.63 ppm, appears as a singlet with ^{195}Pt satellites. The $^{195}Pt-H$ coupling constant value, 1645 Hz, is, to the best of our knowledge, the largest ever reported,¹² and suggests a very strong Pt-H bond. Accordingly, complex **5** shows a remarkable stability both in solution and in the solid state. The extra stability and the large Pt-H coupling constant may be attributed to the influence of the substituents on the platinum atom. Platinum(II) hydride complexes with nitrogen ligands are extremely rare probably due to an intrinsic lability. In previous papers we have found that the presence of a $Pt\cdots H-C$ interaction profoundly affects the behaviour of hydrido species derived from bipyridine

ligands.¹² In particular, the [Pt(N,N,C)H] complex derived from 6-benzyl-2,2'-bipyridine (complex **6**, which is unable to give Pt---H pseudo-axial interactions) is extremely unstable and reactive, whereas the corresponding complexes derived from 6-(1-methylbenzyl)-2,2'-bipyridine (complex **7**) and 6-(1,1-dimethylbenzyl)-2,2'-bipyridine (complex **8**), show increased stabilities. Complex **8**, having a methyl in a pseudo axial position regardless of the conformation of the ring, is extremely stable, even in solution in the presence of moisture and air.



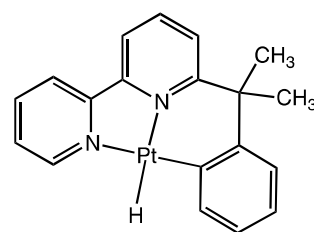
6 (unstable)

Complex **6** rapidly decomposes in solution and in the solid state.
 $^1J_{\text{Pt-H}} = 1600 \text{ Hz}$.



7 (fairly stable)

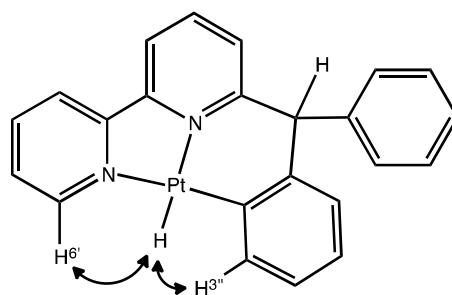
Complex **7** is fairly stable in solution and in the solid state.
 $^1J_{\text{Pt-H}} = 1606 \text{ Hz}$.



8 (very stable)

Complex **8** is stable both in solution and in the solid state even for prolonged times.
 $^1J_{\text{Pt-H}} = 1628 \text{ Hz}$.

It should be pointed out, however, that kinetic factors can play a role because a relatively bulky substituent above the metal may provide a certain degree of inertness.^{12a} In order to confirm the proposed structure for **5** an NOE difference ^1H NMR experiment showed a clear NOE contact between the hydride signal and the two doublets at 9.40 and 7.89 ppm, assignable to the H_6 and $\text{H}_{3''}$, *i.e.* the hydrogen atoms adjacent to the hydride ligand.



Complex **5**, NOE contacts

The chemistry of these complexes is almost unexplored, but very promising. The interaction of complex **8** with various proton donors has been recently investigated by some of us, giving the first example of hydrogen bonding to a metal atom in the presence of hydride ligand.²³

DFT calculations

Calculations using Density Functional Theory (DFT) were performed on complexes **1** and **2**, [Pd(L-H)(Cl)] and [Pt(L-H)(Cl)]. The results obtained using pseudopotentials and ZORA approximation were compared with the solid state structure of complex **2**, obtained from X-ray diffraction. Moreover, the performances obtained by Firefly and ORCA qc packages using the ECP approach were tested.

Table 2: DFT optimized bond distances (Å) and angles (deg) for complex **2**.

	RX	firefly-ecp	orca-ecp	orca-zora
Pt1-Cl1	2.3144(9)	2.3148	2.3150	2.3000
Pt1-N1	2.101(3)	2.1264	2.1243	2.1024
Pt1-N7	2.000(3)	2.0203	2.0205	2.0061
Pt1-C14	2.012(4)	2.0022	2.0025	1.9990
C6-C7	1.4710	1.4751	1.4752	1.4727
N1-Pt1-N7	80.03(12)	79.31	79.35	79.79
N7-Pt1-C14	93.05(13)	94.27	94.25	94.13
C14-Pt1-Cl1	93.26(11)	93.63	93.59	93.29
Cl1-Pt1-N1	94.37(9)	93.05	93.07	93.07
N7-Pt1-Cl1	173.02(9)	172.01	172.06	172.46
N1-Pt1-C14	166.58(13)	169.35	169.45	169.52

It is readily seen from Table 2 that in general every method gives comparable results in the present context, bond distances and angles are satisfactorily reproduced and errors are seldom greater than 1%. Looking more carefully at the data we can see that ZORA performs slightly better in reproducing the distances, with the exception of the Pt-Cl bond, (however, it should be kept in mind that in the crystal structure a water molecule is present, with an HO-H---Cl distance (2.443 Å) shorter than the sum of Cl and H van der Waals radii (2.84 Å)).

Table 3: ZPE corrected energy differences, in kJ/mol, between the two conformers taking the most stable as reference

	1 M = Pd		2 M = Pt	
	ΔH	ΔG	ΔH	ΔG
firefly-ecp	12.9	15.4	14.7	9.2
orca-ecp	5.9	5.6	6.4	7.1
orca-zora	15.5	16.0	9.1	10.4

The terdentate complexes **1** and **2** were also investigated from the energetic point in order to evaluate the differences between the two available conformations. The metal centre is expected to play a non-negligible role and stabilize the axial conformer by M---H interaction with the H_{ortho} of the non metallated phenyl ring.

In Table 3 are reported the ZPE corrected ΔH and ΔG values between the conformers. From the data it can be confirmed that the conformer with the phenyl ring in axial position is more stable by ca. 10 kJ/mol, a result is not completely unexpected.

The distance between the metal and the H_{ortho} proton of the axial phenyl can be extracted from the optimized geometries obtaining is 2.7163 Å in **1**-ax and 2.7875 Å in **2**-ax. These values are below the sum of the van der Waals radii confirming the presence of this interaction.

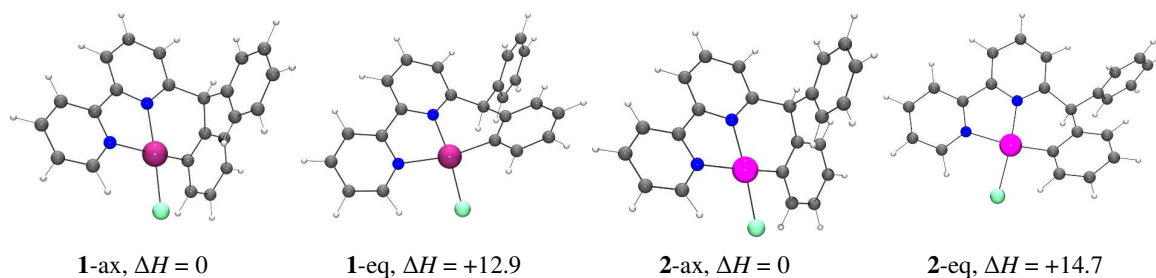


Figure 2: Equilibrium geometries (RI-JONX/PBE0/def2-SVP with ZORA) of the axial (ax) and equatorial (eq) conformers for complex **1** and **2**. Enthalpy differences in kJ/mol are reported, taking the axial isomer – i.e. the most stable one – as reference.

The ring-flipping of the boat conformation was studied by means of DFT calculations. The transition state (TS) search was carried out for complexes **1** and **2** in the gas phase at 298.15 K and the structures obtained are shown in Fig. 3. The computed activation energy for the interconversion is 23.8 and 25.4 kJ/mol for **1** and **2**, respectively.

The structures of the located TSs are characterized by an extended planarity, in fact the biggest deviation from the best plane calculated through N7, C11, C13 and C14 is found for the metal atom itself (0.23 and 0.21 Å respectively for **1**-TS and **2**-TS) while the other five atoms are almost coplanar.

The free phenyl rings in the TS geometry is perpendicular to the above mentioned plane showing angles close to 90 degrees, i.e. 88.73 for **1**-TS and 89.82 for **2**-TS.

The increased planarity of the 6-membered ring at the TS affects also bond distances and angles: the latter become wider while the former elongate. One last thing to be noted regards the N1-M-C14 angle that has nearly the same value in the axial/equatorial couple but during the flip changes side; in other words, if we assume that in the axial conformer the C14 atom is above the coordination plane we will find it below in the equatorial one.

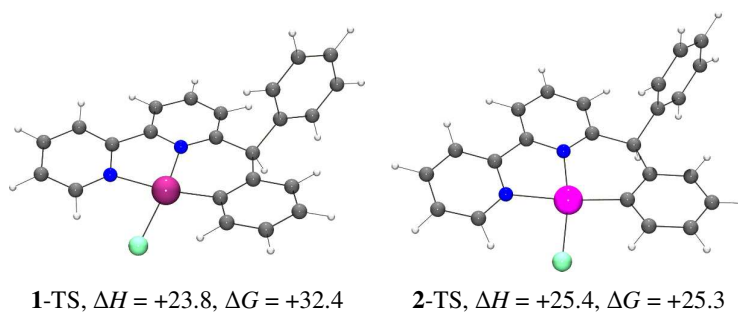
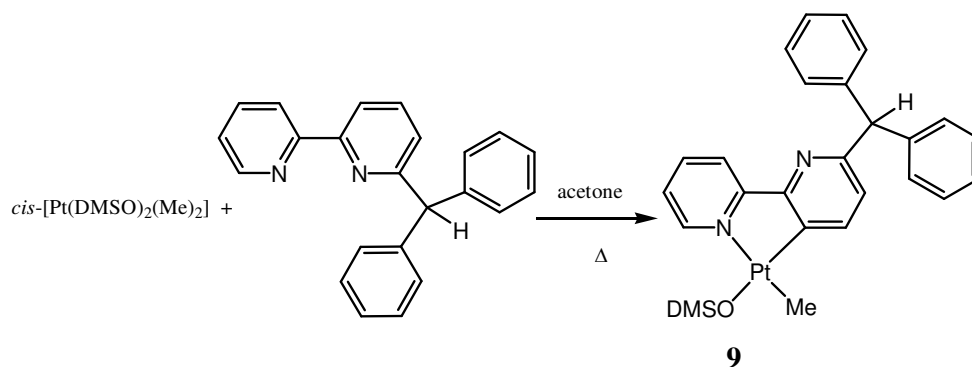


Figure 3: Equilibrium geometries (PBE0/def2-SVP) of the transition states relative to the interconversion between the two conformers of complex **1** and **2**. Enthalpy and Gibbs' free energy differences in kJ/mol are reported, taking the axial isomer – i.e. the most stable one – as reference.

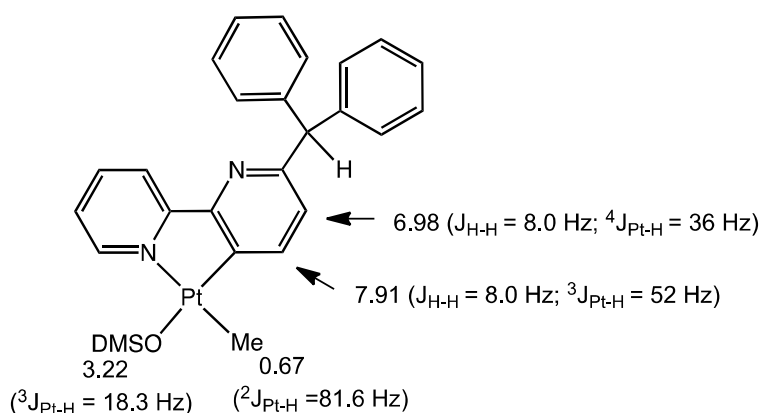
Rollover cyclometalation

The factors governing the regioselectivity of the C-H bond activation, either in intra- or inter-molecular processes, are not completely understood. Under certain conditions, activation of the pyridine C³-H bond may occur, following the so-called “rollover” cyclometalation, which is an unusual behaviour rarely shown by bidentate heterocyclic ligands.^{3, 24}

In the case of LH, reaction with the electron-rich Pt(II) complex [PtMe₂(DMSO)₂] in refluxing acetone gave the rollover complex **9**, [Pt(L-H)(Me)(DMSO)], as the only product, in high yield (ca. 90%).



Characterization of complex **9** is based on analytical and NMR data: an AX system (with satellites) in the aromatic region indicates activation of the inner pyridine ring. The signals, at 7.91 ($J_{\text{H-H}} = 8.0$ Hz; $^3J_{\text{Pt-H}} = 52$ Hz; H_4) and 6.98 ppm ($J_{\text{H-H}} = 8.0$ Hz; $^4J_{\text{Pt-H}} = 36$ Hz; H_5) are diagnostic for this uncommon behaviour. In addition, the DMSO and the coordinated methyl signals are both coupled to ^{195}Pt (δ 0.67 ppm, $^2J_{\text{Pt-H}} = 81.6$ Hz, Pt-Me; δ = 3.22 ppm, $^3J_{\text{Pt-H}} = 18.3$ Hz, Pt-DMSO). The ^{195}Pt - ^1H coupling constant value of the DMSO protons indicate an S-bonded DMSO, coordinated *trans* to a C atom.²⁵



The synthesis of complex **9** is a further confirmation that metal-mediated activation of C-H bonds is a complex field. Several factors compete in the regioselectivity of the process: in this case, among the others, the different stability of classical cyclometalated (a terdentate N,N,C complex, with a six-membered cycle and a weak Pt---H-C interaction) and the rollover complexes (an N,C chelated species with a planar five-membered cycle). However, the driving force may be essentially kinetic: in the formation of complexes **1** and **2** removal of HCl may be reversible, whereas removal of CH_4 in the formation of **9** is almost certainly

irreversible. It is likely that different reaction mechanisms are in competition in the C-H bond activation process.

The rollover process has received growing interest in recent years with potential applications in organic synthesis, mediated by Pt(II)²⁶ and Pd(II)²⁷ complexes, and very recently, in homogeneous catalysis, with a series of different processes promoted by Pd(II),²⁸ Rh(III)²⁹ and Ru(II).³⁰

Conclusions

New terdentate N,N,C Pd(II) and Pt(II) complexes, containing a cyclometalated 6-substituted-2,2'-bipyridine, have been synthesized and characterized. The complexes contain a six-membered N,C metallacycle with a stereogenic carbon atom directly generated by C-H bond activation. The metallacycles adopt a boat like conformation, as demonstrated, in the case of the platinum complex, by X-ray diffraction, and confirmed by DFT calculations. These studies also suggest the presence of a weak metal--H interaction that stabilizes one of the two possible conformers. Likely due to the extra stability furnished by the phenyl substituent it was possible to isolate the stable platinum(II) hydride [Pt(N,N,C)H]. Organometallic platinum(II) hydrides with only nitrogen ligands are extremely rare; only in the presence of a group in axial position a few of these species have shown to be fairly stable both in solution and in the solid state. Due to their rarity, the chemical behaviour of these complexes is almost unexplored. The scarce studies on their reactivity, however, seem very promising, having recently given the first example of hydrogen bonding to a metal atom in the presence of hydride ligand.²³

Finally, regioselectivity of C-H bond activation in these 2,2'-bipyridines complexes may be controlled by using electron-rich platinum(II) derivatives, such as [Pt(Me)₂(DMSO)₂], to afford the less common rollover complex [Pt(L-H)Me(DMSO)] where activation of the pyridine C³-H bond occurs, in place of the more common ortho-metallation.

Acknowledgements

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Experimental Section

All the solvents were purified and dried according to standard procedures.³¹ Elemental analyses were performed with a Perkin-Elmer elemental analyzer 240B by Mr. Antonello Canu (Dipartimento di Chimica e Farmacia, Università degli Studi di Sassari, Italy).

¹H NMR spectra were obtained on Varian VXR 300 and Mercury VX 400, or on a Bruker Avance III 400 spectrometers.

Chemical shifts are given in ppm relative to internal TMS. ¹H NOE difference, ¹H-¹H-COSY and ¹H-¹³C HSQC experiments were performed by means of standard pulse sequences.

DFT calculations

DFT calculations were carried out using Firefly QC package,³² which is partially based on the GAMESS (US) source code,³³ and ORCA. Geometry optimizations, using slightly tighter convergence criteria, were carried out using the PBE0 hybrid functional developed by Perdew, Burke, and Ernzerhof³⁴ and modified in its hybrid version by Adamo and Barone,³⁵ with ZORA³⁶ using the SV-ZORA basis sets³⁷ along with the RI-JONX approximation as implemented in the ORCA 3.0.3 package.³⁸ Def2-SVP basis sets of Ahlrichs and co-workers³⁹ were used with Firefly, as found in the EMSL basis set library,⁴⁰ for all lighter atoms (H, C, N and Cl), for palladium and platinum the same basis set was integrated with an effective core potential (ECP) removing 28 and 60 core electrons, respectively. Harmonic analysis at the same level of theory (RI-JONX/PBE0/def2-SVP or PBE0/def2-SVP) was performed on each of the equilibrium geometries to confirm their minimum nature on the potential energy surface (i.e., the absence of imaginary frequencies).

Crystal structure determination of 2

Single crystals of C₂₃H₁₈ClN₂O_{0.5}Pt (**2**) were grown from CHCl₃-di-isopropyl ether. A suitable crystal was selected and mounted on a glass fibre with Fromblin oil and placed on an Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 150(2) K during data collection. Using Olex2,⁴¹ the structure was solved with the ShelXT⁴² structure solution program using Direct Methods and refined with the ShelXL⁴² refinement package using Least Squares minimisation.

Crystal Data for C₂₃H₁₈ClN₂O_{0.5}Pt (*M* = 560.93 g/mol): monoclinic, space group I2/a (no. 15), *a* = 15.5280(2) Å, *b* = 13.72430(10) Å, *c* = 17.6847(2) Å, *β* = 100.5210(10)°, *V* = 3705.44(7) Å³, *Z* = 8, *T* = 150(2) K, *μ*(MoK α) = 7.731 mm⁻¹, *D*_{calc} = 2.011 g/cm³, 54517 reflections measured (4.686° ≤ 2 θ ≤ 64.706°), 6348 unique (*R*_{int} = 0.0537, *R*_{sigma} = 0.0374)

which were used in all calculations. The final R_1 was 0.0262 ($I > 2\sigma(I)$) and wR_2 was 0.0780 (all data).

The asymmetric unit contains the complex and half molecule of water. There is eight times all this in the unit cell. Water O1 sits on a two fold axis on special position e. The hydrogen was located on this water and refined with DFIX and DANG restraints to give it and its symmetry equivalent hydrogen, reasonable bond lengths and angles of a water molecule. H1 was given thermal parameter U_{iso} 1.5 times the U_{eqiv} of the parent O1. It forms hydrogen bonds with the chloride Cl forming H-bonded bridges between symmetry related complexes.

X-ray crystallographic data in CIF format have been deposited at the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 1409374.

Preparations

2-(1-phenylbenzyl)pyridine N-oxide

To a solution of 2-(1-phenylbenzyl)pyridine (10.03 g, 0.041 mol) in acetic acid (20 mL) were added 14 mL of hydrogen peroxide 30 % (15.74 g, 0.139 mol). The solution was heated to 70°C for 3 h under vigorous stirring, then a second amount of hydrogen peroxide was added (14 mL). The solution was heated for further 10 h at 70°C, then it was concentrated to small volume, treated with 10 % NaOH in order to obtain an alkaline mixture. The organic product was extracted with CH_2Cl_2 (3x50 ml), treated with Na_2SO_4 , filtered and evaporated to dryness. The white solid was treated with diethyl ether and filtered off, to give the N-oxide with a 60% yield. ^1H NMR (CDCl_3) 2-(1-phenylbenzyl)pyridine (for comparison): 5.71 (s, 1H, CHPh_2), 7.14-7.30 (12H, H(Ph), H_3 , H_5), 7.60 (ddd, 1H, H_4), 8.60 (ddd, 1H, H_6).

^1H NMR (CDCl_3) 2-(1-phenylbenzyl)pyridine N-oxide: 6.33 (s, 1H, CHPh_2), 6.96 (t, 1H, H_3 or H_5), 7.11 (d, 4H, H *orto*), 7.18 (t, 2H, H *para*), 7.23-7.34 (m, 6H, H *meta* (4H), H_3 or H_5 , H_4), 8.27 (t, 1H, H_6).

2-cyano-6-(1-phenylbenzyl)pyridine

To a solution of the N-oxide of 2-(1-phenylbenzyl)pyridine (6.30 g, 0.0241 mol) in 135 mL of anhydrous CH_2Cl_2 were added, under a nitrogen atmosphere, 3.45 mL of trimethylsilyl nitrile (2.52 g, 0.0254 mol) and 2.20 mL of N,N dimethylcarbamoyl chloride (2.53 g, 0.0235 mol). The solution was stirred at room temperature for 3 days, after which was refluxed for 9 h. The solution was cooled down to room temperature and an aqueous 10% solution of

Na₂CO₃ was added (100 mL). The N-oxide was extracted with CH₂Cl₂ (3 x 60 ml); the solution was dried with anhydrous Na₂SO₄, filtered and evaporated to dryness, to give the product as a white solid, Yield 50%. ¹H NMR (CDCl₃): 5.72 (s, 1H, CHPh₂), 7.15 (d, 4H, H Ph *ortho*), 7.25-7.36 (m, 7H, H Ph *meta* + *para*, H₃ or H₅), 7.56 (d, 1H, H₅ or H₃), 7.75 (t, 1H, H₄).

Synthesis of 6-(1-phenyl)benzyl-2,2'-bipyridine, L

The ligand L, 6-(1-phenyl)benzyl-2,2'-bipyridine, was prepared by reaction in autoclave of 2-cyano-6-(1-phenylbenzyl)pyridine (3.05 g, 11.3 mmol) with acetylene (14 bar) in anhydrous toluene (100 mL) in the presence of Bönnemann catalyst ([Co(Cp)(COD)], 0.302 g, 0.0013 mol). After 2 days at 130°C the reaction mixture was filtered, and the ligand was purified by a double extraction, with aqueous HCl (5% solution) and NaOH/diethyl ether. Yield 50 %.

Anal. Calcd for C₂₃H₁₈N₂ · 0.25H₂O: C, 84.50; H, 5.70; N, 8.57. Found: C, 84.33; H, 6.02; N, 8.23 %. ¹H NMR (CDCl₃): 5.74 (s, 1H, CHPh₂), 7.22 (dd, 1H, J_{H-H} = 7.9 Hz, J_{H-H} = 1.1 Hz, H₅), 7.24 (m, 2H, H_{para} Ph, part. overlapping), 7.28 (m, 4H H_{ortho} Ph, part. overlapping), 7.32 (m, 4H, H_{meta} Ph, part. overlapping), 7.26 (ddd, 1H, H₅), 7.79 (t, 1H, J_{H-H} = 7.9 Hz, H₄, part. overlapping), 7.80 (td, 1H, J_{H-H} = 7.8 Hz, J_{H-H} = 1.5 Hz, H_{4'}, part. overlapping), 8.31 (dd, 1H, J_{H-H} = 7.9 Hz, J_{H-H} = 0.9 Hz, H₃), 8.37 (dt, 1H, J_{H-H} = 7.9 Hz, J_{H-H} = 0.9 Hz, H_{3'}), 8.66 (ddd, 1H, J_{H-H} = 4.8 Hz, J_{H-H} = 1.7 Hz, J_{H-H} = 0.9 Hz H₆). ¹³C NMR (CDCl₃): 59.40 (CHPh₂), 118.59 (C₃), 121.41 (C_{3'}), 123.57 (C₅), 123.88 (C₅), 126.41 (C_{para}), 128.29 (C_{meta}), 129.45 (C_{ortho}), 136.81 (C_{4'}), 137.28 (C₄), 143.18 (C_{ipso}), 148.97 (C_{6'}), 155.57 (C₂ or C_{2'}), 156.38 (C₂ or C_{2'}), 162.12 (C₆).

[Pd(L-H)Cl], 1

To a solution of Na₂[PdCl₄]·4H₂O (113,5 mg, 0,310 mmol) in water (20 mL) were added under stirring 100 mg of L (0.310 mmol) and 5 mL of 1M aqueous HCl. The mixture was stirred at room temperature for 2 days. The pale yellow precipitate formed was filtered off, washed with diethyl ether and recrystallized from dichloromethane and diethyl ether, to give the analytical sample as a pale yellow solid. Yield 70 %. M.p. 227-231°C (dec.). Anal. Calcd for C₂₃H₁₇ClN₂Pd: C, 59.63; H, 3.70; N, 6.05. Found: C, 57.74; H, 3.80; N, 5.88 %.

Conductivity: Λ_M(7.5 · 10⁻⁴M, acetone)= 1.8 Ω⁻¹cm² mol⁻¹. ¹H NMR (CDCl₃): 5.75 (s, 1H, CH), 6.98 (td, 1H, J_{H-H} = 7.9 Hz, J_{H-H} = 1.5 Hz, H_{4'}), 7.07 (td, 1H, J_{H-H} = 7.8 Hz, J_{H-H} = 1.4

Hz, H_{5'}), 7.20 (m 1H, H Ph *para*), 7.22 (m, 1H, H_{6'}), 7.29 (m, 2H, H Ph *meta*), 7.57 (d, 2H, J_{H-H} = 7.7 Hz, H Ph *ortho*), 7.61 (m, 1H, H_{5'}), 7.84 (dd, 1H, J_{H-H} = 7.9 Hz, J_{H-H} = 1.4 Hz, H₅), 8.01 (dd, 1H, H_{3'}), 8.07-8.04 (m, 3H, H₃, H_{3'}, H_{4'} (overlapping signals)), 8.08 (t, 1H, partially overlapping, H₄), 9.31 (d, 1H, J_{H-H} = ca 5.0 Hz, H_{6'}).

[Pt(L-H)Cl], 2

To a solution of K₂[PtCl₄] (128.7 mg, 0.310 mmol) in H₂O (20 mL), were added 100.0 mg of L (0.310 mmol) and 2 mL of 1M aqueous di HCl. The mixture was heated on a water bath for several days, until the solution was colourless, and then cooled; the yellow precipitate was filtered off, washed with water, ethanol and diethyl ether and finally recrystallised from dichloromethane and diethyl ether to give the analytical sample as a yellow solid. Yield 95 %. M.p. 212-214°C (dec). Anal. Calcd for C₂₃H₁₇ClN₂Pt: C, 50.05; H, 3.10; N, 5.08. Found: C, 49.94; H, 2.91; N, 4.99 %. ¹H NMR (CD₂Cl₂): 5.67 (s, 1H, CH(Ph)₂), 7.26-6.98 (m, 4H, H_{6'}, H_{5'}, H_{4'}, H *para* Ph), 7.21 (m, 2H, H *meta* Ph), 7.52 (m, 2H, H *ortho* Ph), 7.68 (ddd, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 5.6 Hz, J_{H-H} = 1.3 Hz, H_{5'}), 7.79 (dd sat, 1H, J_{H-H} = 7.8 Hz, J_{H-H} = 1.3 Hz, ³J_{Pt-H} ca. 27 Hz, H_{3'}), 7.93 (dd sat, 1H, H₅, J_{H-H} = n.r., ⁴J_{Pt-H} ca. 10 Hz), 8.00-8.06 (m, 2H, H₃, H_{3'}), 8.11 (td, 1H, H_{4'}), 8.12 (t, 1H, J_{H-H} = 7.9 Hz, J_{H-H} = 1.7 Hz, H₄), 9.62 (ddd sat, 1H, J_{H-H} = 5.6 Hz, J_{H-H} = 1.6 Hz, J_{H-H} = 0.8 Hz, ³J_{Pt-H} = ca. 13 Hz, H_{6'}).

[Pt(L-H)H], 5

A suspension of [Pt(L-H)Cl], 2, (150.5 mg, 0.272 mmol) in 50 mL of freshly distilled THF was heated to reflux under argon atmosphere and vigorous stirring. NaBH₄ (10.8 mg, 0.285 mmol) was added at intervals of 30', then the mixture was stirred for other 2 h. The suspension was cooled on a water/ice bath, then filtered over celite to give a solution which was concentrated to small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and dried, to give the analytical sample as a red solid. Yield 45 %, m.p. 220 °C. Anal. Calcd. For C₂₃H₁₈N₂Pt · H₂O: C, 51.59; H, 3.76; N, 5.23. Found C, 51.49; H, 3.92; N, 4.88 %. ¹H NMR (Me₂CO-*d*₆): 9.40 (d sat, 1H, J_{H-H} = 5.4 Hz; ³J_{Pt-H} = 25 Hz H_{6'}), 8.42 (d, 1H, J_{H-H} = 7.8 Hz), 8.34-8.28 (m, 2H), 8.23 (t, 1H, J_{H-H} = 7.8 Hz, H₄), 8.8-8.2 (m, 2H), 7.90 (d, 1H, J_{H-H} = 7.8 Hz), 7.63 (ddd, 1H, J_{H-H} = 1.4 Hz, J_{H-H} = 5.5 Hz, J_{H-H} = 6.9 Hz, H_{5'}), 7.15-7.10 (m, 3H), 7.03 (t, 1H, J_{H-H} = 5.2 Hz), 6.79 (td, 1H, J_{H-H} = 1.4 Hz, J_{H-H} =

7.1 Hz), 6.69 (td, 1H, $J_{\text{H-H}} = 1.6$ Hz, $J_{\text{H-H}} = 7.3$ Hz), 5.91 (s, 1H, CH benzylic), - 13.63 (s sat, 1H, $J_{\text{Pt-H}} = 1646$ Hz, H-Pt).

[Pt(L-H)(Me)(DMSO)] **9**

To solution of *cis*-[PtMe₂(DMSO)₂] (76.2 mg, 0.199 mmol) in acetone (ca 15 mL) was added a slight excess of L under nitrogen atmosphere (67.8 mg, 0.21 mmol). The mixture was heated to reflux for 3 h, then it was concentrated to small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and dried, to give the analytical sample as a green-yellow solid. Yield 90 %, m.p. 221 °C. Anal. Calcd for C₂₆H₂₆N₂OPtS: C, = 51.22; H, 4.30; N, 4.60. Found: C, 51.49; H, 3.92; N, 4.88 %.

¹H NMR (CDCl₃): 9.65 (d sat, 1H, $J_{\text{H-H}} = 5.5$ Hz; $^3J_{\text{Pt-H}} = 15$ Hz), 8.21 (d, 1H, $J_{\text{H-H}} = 6.7$ Hz), 7.91 (d sat, 1H, $J_{\text{H-H}} = 8.0$ Hz; $^3J_{\text{Pt-H}} = 52$ Hz; H₄), 7.85 (td, 1H, $J_{\text{H-H}} = 7.9$ Hz, $J_{\text{H-H}} = 1.5$ Hz), 7.36 – 7.1 (m, 12 H), 6.98 (d sat, 1H, $J_{\text{H-H}} = 8.0$ Hz; $^3J_{\text{Pt-H}} = 36$ Hz; H₅), 5.60 (s, 1H, benzylic CH), 3.22 (s sat, 6H, $^3J_{\text{Pt-H}} = 18.3$ Hz (Me DMSO)), 0.67 (s sat, 3H, $^2J_{\text{Pt-H}} = 81.9$ Hz (Me-Pt)).

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Table of contents entry

Cyclometalation of a new bipyridine ligand gave Pt(II) and Pd(II) complexes containing a stereogenic carbon atom generated by C-H bond activation

